

Manipulating Biogeochemical Processes in an Advective Flow Field: *In Situ* Stabilization of Metals and Radionuclides by Co-Precipitation in Calcite

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Coupled Processes and *In Situ* Stabilization

- *In situ* stabilization results from a transient perturbation of the biogeochemical environment
 - Application of treatment
 - Remobilization of contaminants from less stable form
 - Sequestration in more stable form
- Stabilization ***must*** persist for decades to centuries after active treatment ends
 - Biogeochemical environment will revert to pre-treatment background conditions
 - Coupling between the rates of local biogeochemical processes and the global fluxes



Proposed Stabilization Strategy

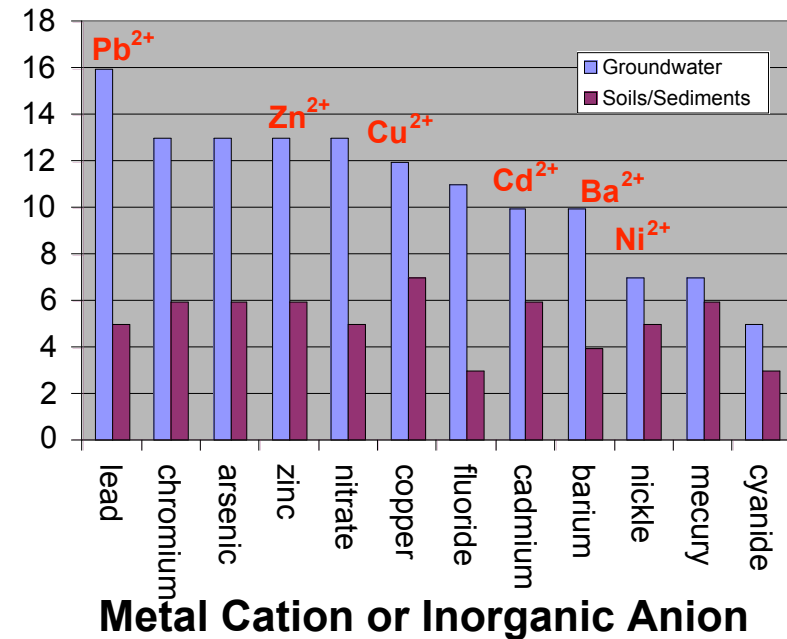
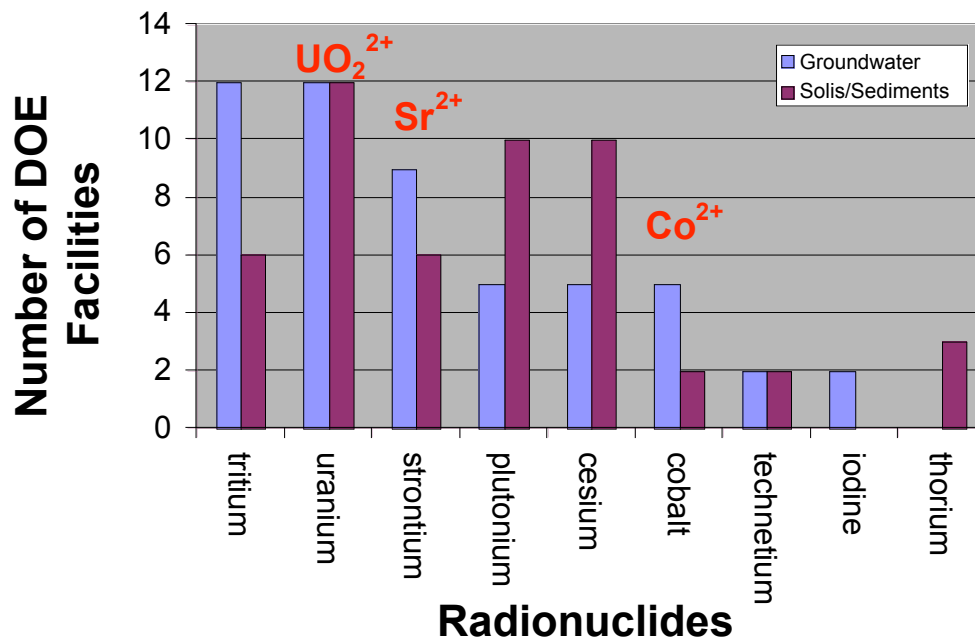
- Manipulate the kinetics of calcite precipitation in an aquifer in order to increase the rate of coprecipitation of divalent metals (eg. $^{90}\text{Sr}^{2+}$, $^{60}\text{Co}^{2+}$, Pb^{2+} , Cd^{2+}) from the aqueous phase.



- Co-precipitation of metals in calcite at arid western sites is compatible with the long term subsurface biogeochemistry



Divalent Metals and Radionuclides are Common at DOE sites



Riley and Zachara 1992

⁹⁰Strontium Contamination

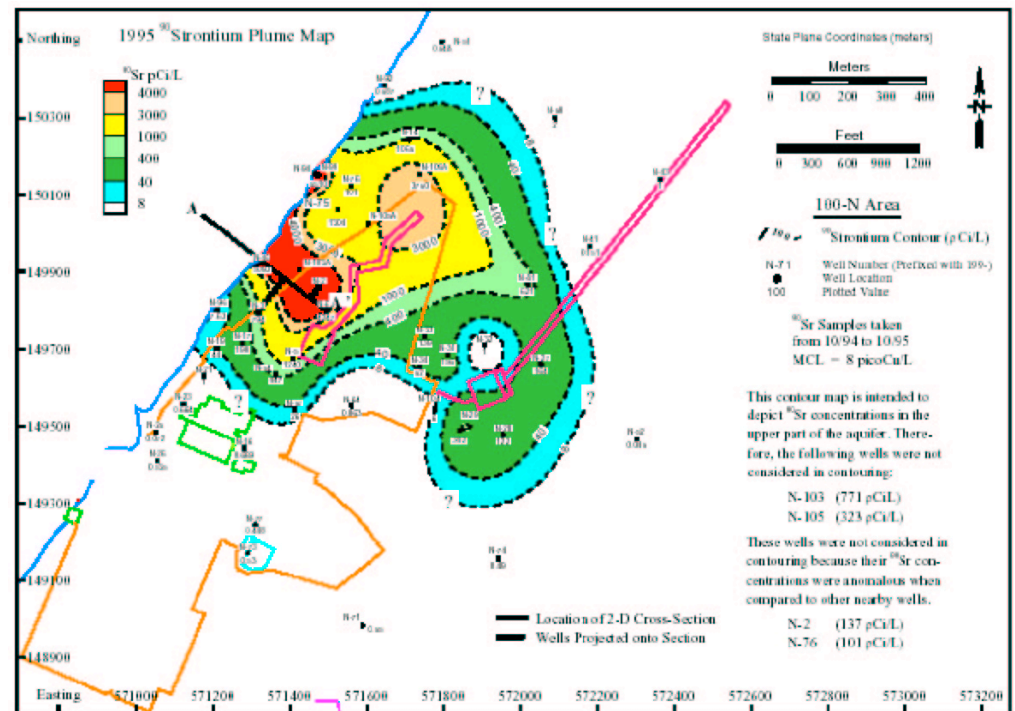
INEEL groundwater, perched water (INTEC)

- Up to 84 pCi L⁻¹ in a 1.6 km² groundwater plume
- Up to 320,000 pCi L⁻¹ in perched water

Hanford soils, groundwater (100N)

- Est in-ground inventory of 75 to 89 Ci
- Groundwater levels up to 6000 pCi L⁻¹

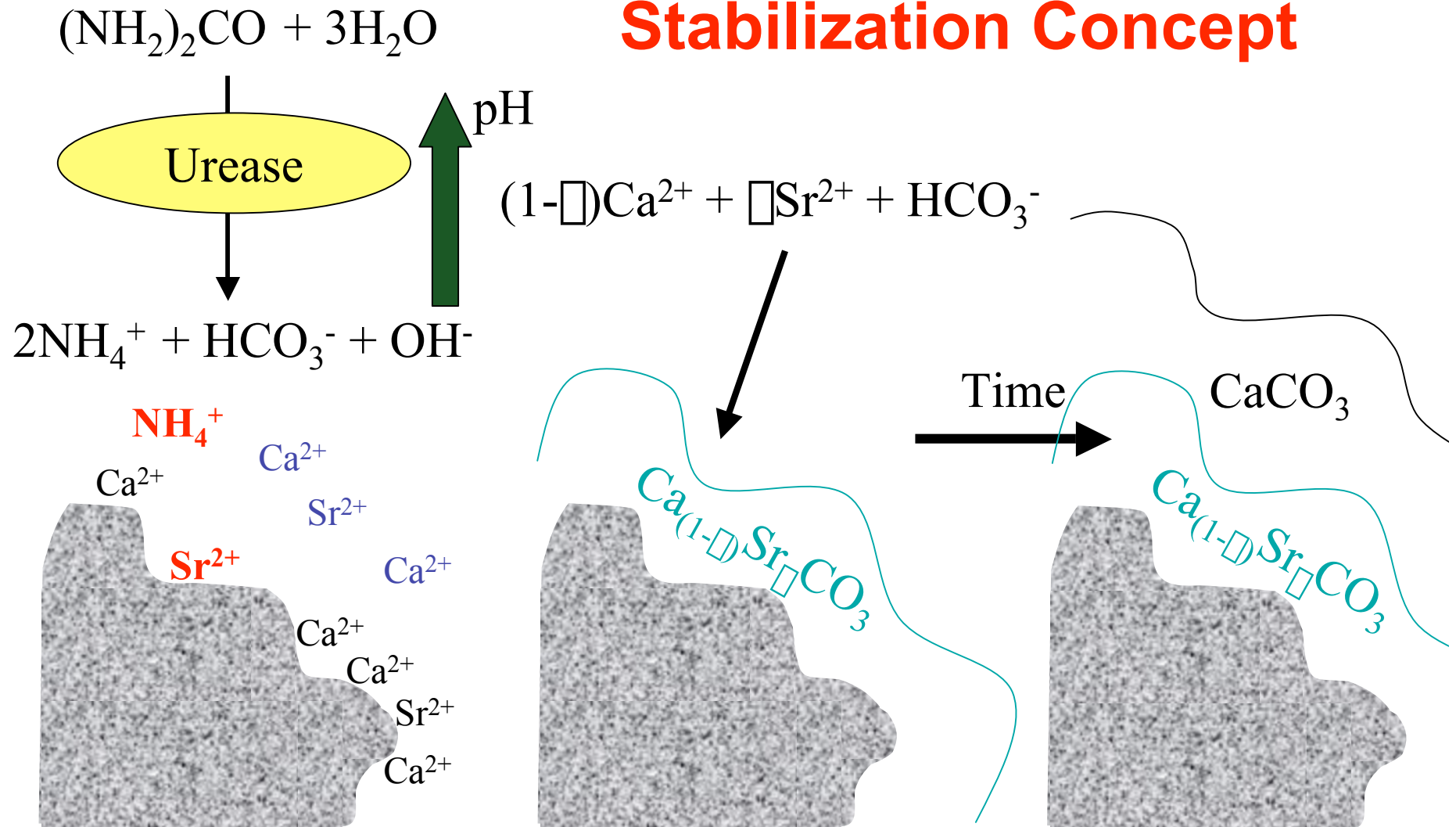
EPA Regulatory Limits for ⁹⁰Sr in drinking water: 8 pCi L⁻¹



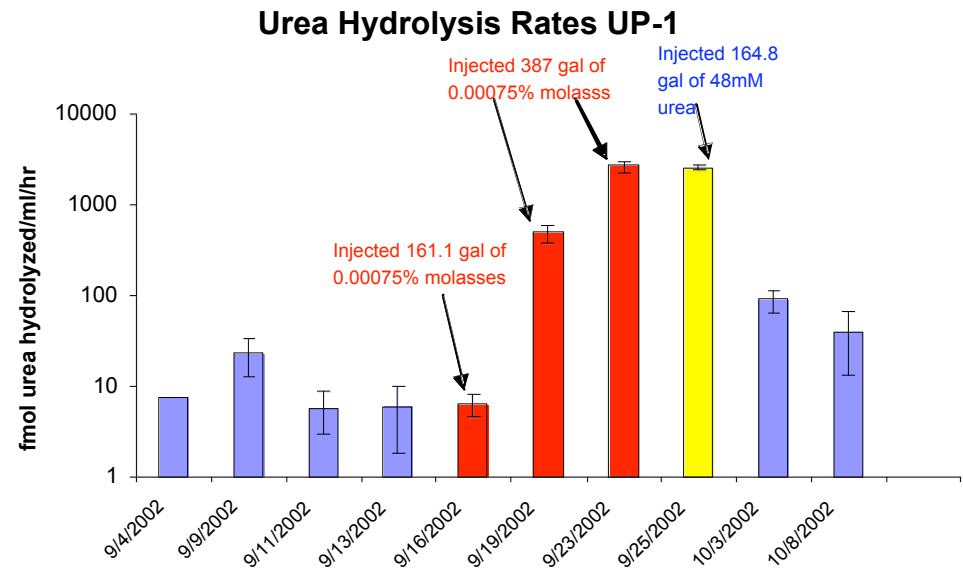
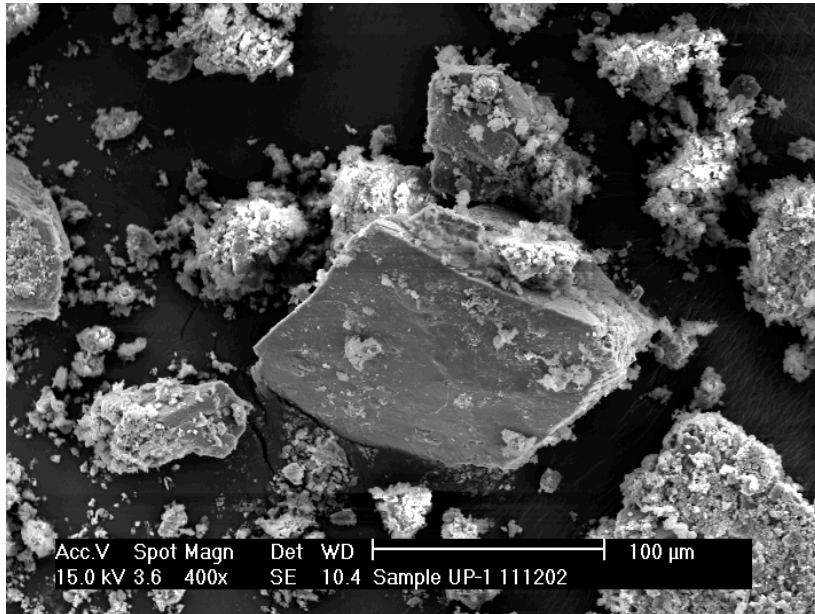
Contaminant inventories are largely associated with the solid media, not the water



In Situ Stabilization Concept

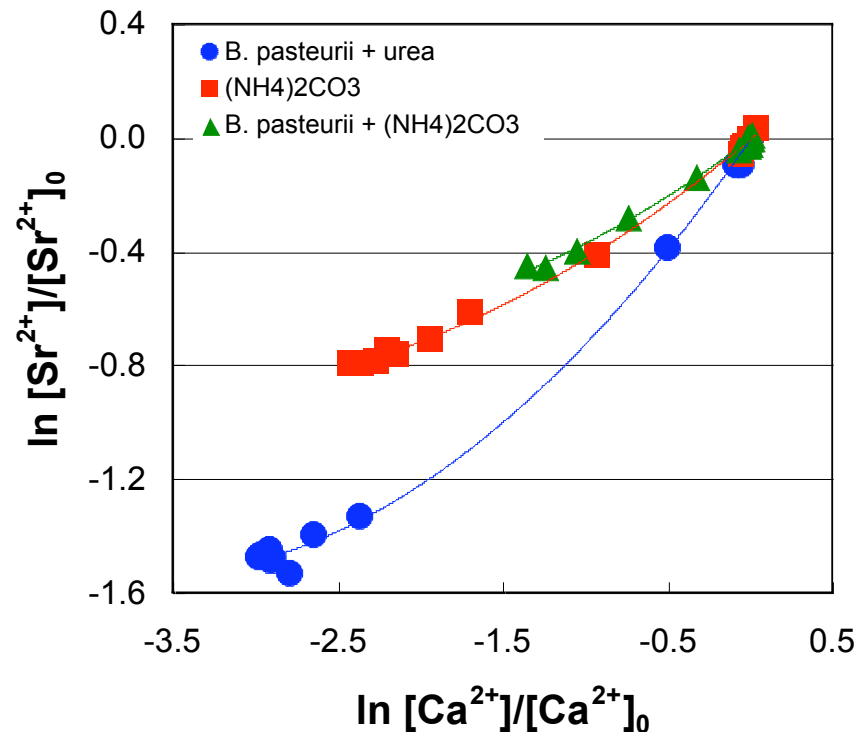


Results to Date (1)



- Demonstrated in laboratory and field the linkage between urea hydrolysis and calcite precipitation.

Results to Date (2)



- Observed that Sr is incorporated into calcite precipitated by urea hydrolyzers, with higher distribution coefficient than in abiotic systems

Snake River Plain Model Aquifer System

| mg L ⁻¹ | | mg L ⁻¹ | |
|-------------------------------|------|-------------------------------|------|
| Ca ²⁺ | 70.1 | Na ⁺ | 25.8 |
| Mg ²⁺ | 10.9 | K ⁺ | 4.0 |
| HCO ₃ ⁻ | 69.8 | Cl ⁻ | 124 |
| NO ₃ ⁻ | 5.2 | SO ₄ ²⁻ | 43.0 |
| pH | 8.15 | ¹ CEC | 1.5 |
| T (°C) | 14 | ² Kd _{Sr} | 5.0 |

¹(meq 100 g⁻¹) ²(mL g⁻¹)

- 6.67 liter total volume (15% porosity)
- 1 liter (1 kg) of water
- 5.67 liter (15.3 kg) of geomedia (CEC only reactivity)
- 2.70 kg liter⁻¹ (grain density)
2.29 kg liter⁻¹ (bulk density)
- React 2 mmoles aqueous urea
- Kinetics
 - 1st order for urea hydrolysis
 - 2nd order chemical affinity for calcite precipitation
- Geochemist's Workbench simulations



Kinetic Model

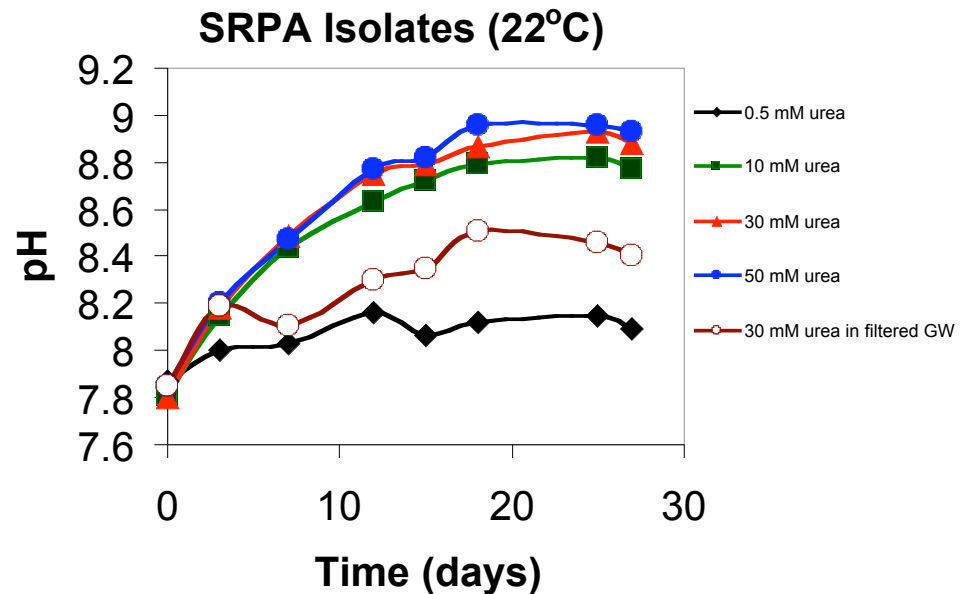
Urea Hydrolysis



$$\frac{d[\text{urea}]_{\text{total}}}{dt} = -k_{\text{urea}}[\text{urea}]$$

$$\frac{d[\text{NH}_4^+]_{\text{total}}}{dt} = 2k_{\text{urea}}[\text{urea}]$$

$$\frac{d[\text{CO}_3^{2-}]_{\text{total}}}{dt} = k_{\text{urea}}[\text{urea}]$$



Kinetic Model

Calcite Precipitation



$$\frac{d[\text{calcite}]}{dt} = k_{\text{calcite}} (S - 1)^2$$

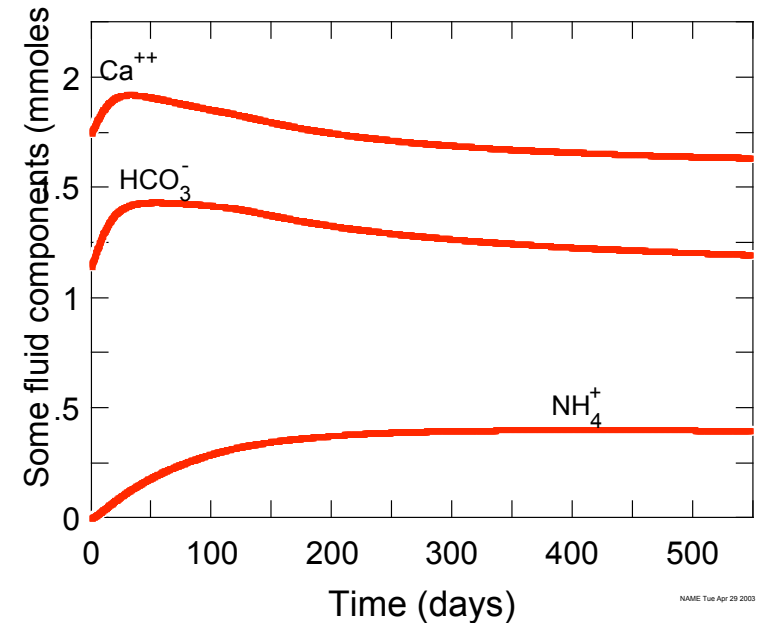
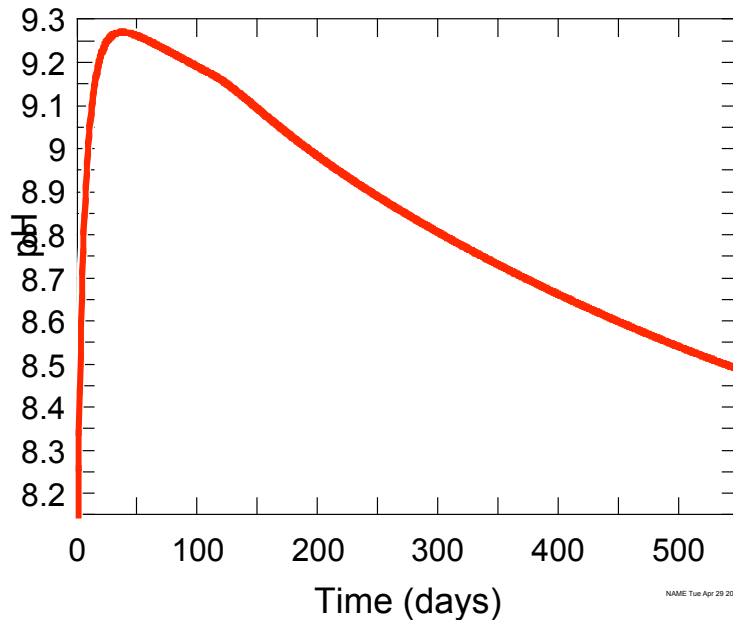
$$S = \frac{Q}{K} = \frac{a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}}{K_{eq}}$$

NETPATH model of McLing (1994) suggests that ~0.3 mmole (net) of calcite precipitate per liter of groundwater as it travels across the INEEL site (~50 years)

$S \rightarrow 2.2$



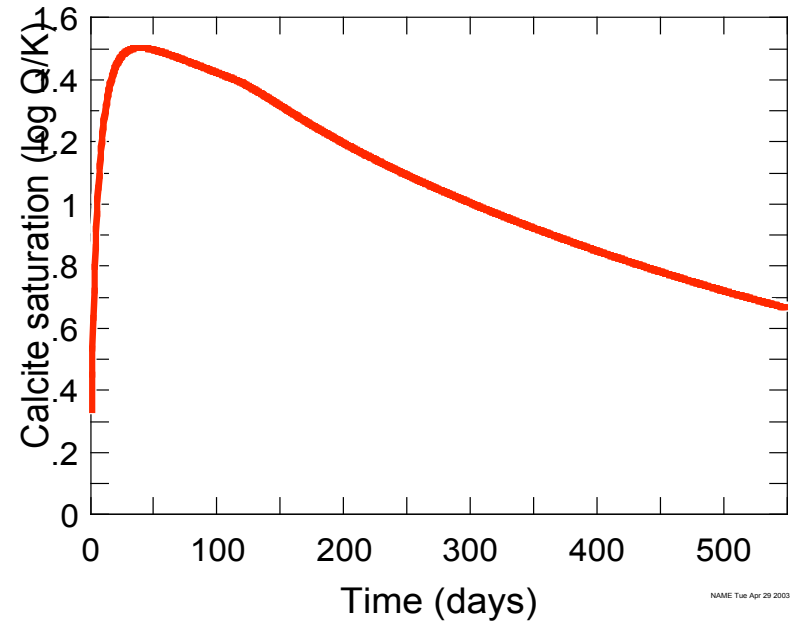
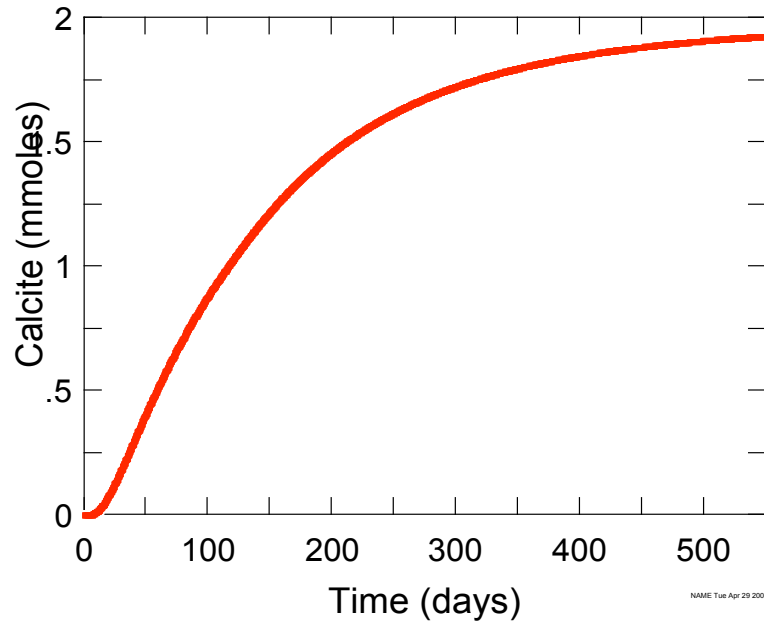
Batch System Calculations (No Transport)



- pH and HCO_3^- initially rises due to urea hydrolysis, then decrease as calcite precipitates.
- Ca^{2+} initially rises due to exchange with NH_4^+ , then decrease as calcite precipitates.



Batch System Calculations (No Transport)

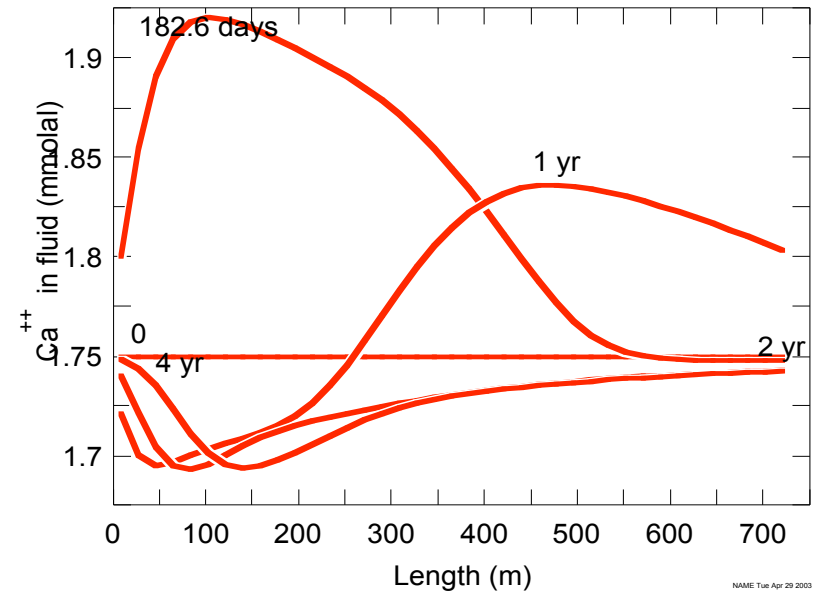
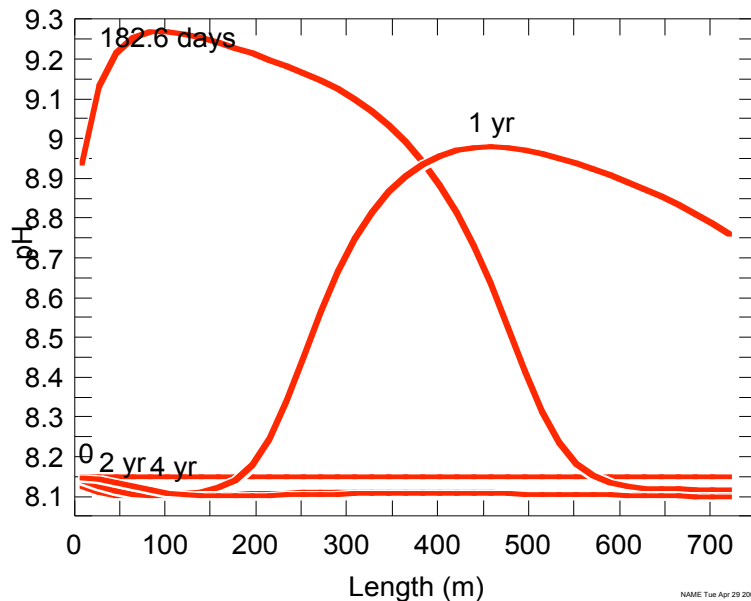


- Hydrolysis of 2 mmol urea results in precipitation of almost 2 mmole of calcite.
- Q/K rises rapidly as urea hydrolyzes faster than calcite precipitates, Q/K falls as the two rates become equivalent.



Reactive Transport

(6 month injection, 1-D, 730 m, 1 pore volume year⁻¹)

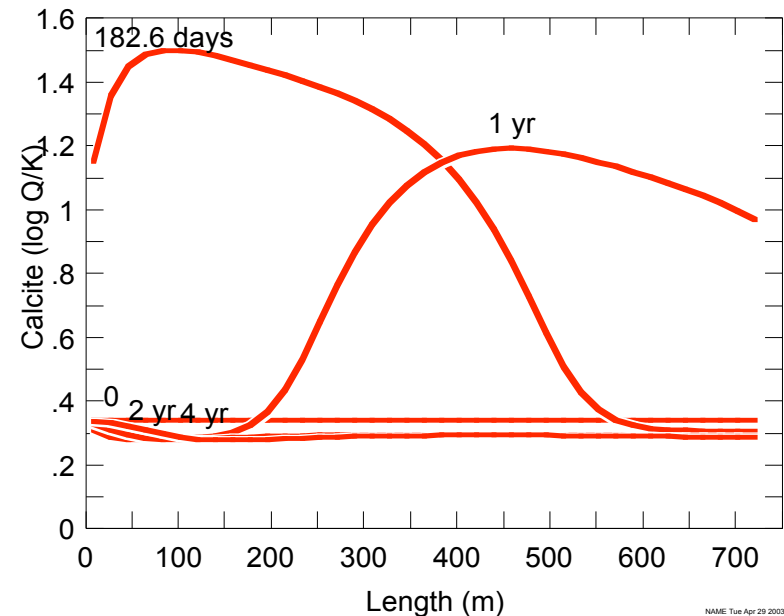
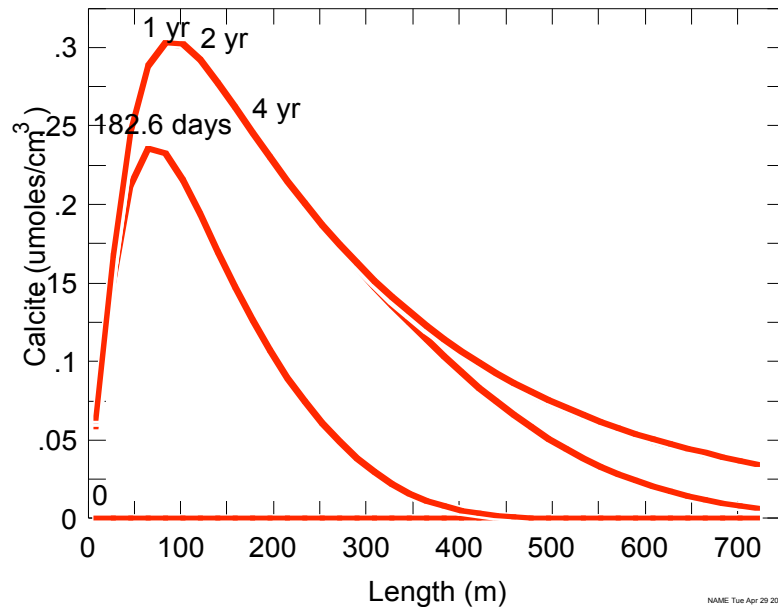


- High pH moves through system. Near ambient pH values return in less than 18 months
- High $[\text{Ca}^{2+}]$ moves through system in early times as NH_4^+ exchanges for Ca^{2+} . During later times low $[\text{Ca}^{2+}]$ moves through system as Ca^{2+} exchanges for NH_4^+



Reactive Transport

(6 month injection, 1-D, 730 m, 1 pore volume year⁻¹)



- Calcite precipitates through the entire regions and is essentially complete within 2 years.
- Q/K is elevated (> 30) during early times and slightly depressed (but > 1) during later times. This condition persists until NH_4^+ is swept from the system (decades).



Summary of Results

- Urea hydrolysis can be used to manipulate *in situ* biogeochemistry and facilitate calcite precipitation
- Process optimization is a trade off between rapidly precipitating calcite (high urea injection concentrations) and long-term calcite stability (low urea injection concentration)



Couple Process Modeling Implications

- Results from batch and advective simulation differ
- Calcite precipitation and biomass development can influence flow field (Is this predicable?)
- Over long time frames process other than cation exchange may become important (e.g., rock weathering?)
- Over long time frames ammonium oxidation may be important (e.g. controlled by O_2 flux?)



Coupled Processes

Experimental Implications

- Field demonstrations are important, but not a good place to develop fundamental understanding.
 - Expensive
 - *In situ* monitoring of chemical parameters is limited
 - Hard to control
 - Impractical to replicate
- Well-controlled and monitored couple process experiments needed to parameterize models

